

Solution for Chapter 4

(compiled by Xinkai Wu, Kip Thorne, Jeff Atwell, Michael Cross, and Huan Yang)

A.

Exercise 4.1 Pressure Measuring Device [by Kip Thorne]

The probability for the meter to be in a (quantum) state with volume ΔV and energy $\Delta \tilde{E}$ (probability measured either using an ensemble of meter&reservoir systems or via the fraction of the time the meter spends in a given state) is given by the meter's Gibbs distribution:

$$\rho = K \exp[(-\Delta \tilde{E} - P \Delta V)/kT] ;$$

or equivalently

$$\ln \rho = (-\Delta \tilde{E} - P \Delta V)/kT + \text{constant} .$$

Here K is the normalization constant and P and T are the reservoir's pressure and temperature.

Suppose that the reservoir plus meter has total energy \tilde{E}_o , volume \tilde{V}_o , and number of particles N_o ; and the meter plus reservoir is a closed system. Then by energy and volume conservation, when the meter has volume ΔV and energy ΔE , the reservoir has volume $V_r = \tilde{V}_o - \Delta V$ and energy $E_r = \tilde{E}_o - \Delta E$. Denote by $\mathcal{N}_r(\tilde{E}_r, V_r)$ the total number of states of the reservoir that have energy E_r , volume V_r and particle number N_r , and similarly $\mathcal{N}_m(\Delta E, \Delta V)$ for the meter. (The meter might not be made of the same kind of particles as the reservoir; it might, for example, just be a mass-spring system that can be heated; the only variables we care about for it are energy and volume.) Then the probability ρ is proportional to the number of states for the reservoir:

$$\rho \propto \mathcal{N}_r(E_o - \Delta E, V_o - \Delta V, N_o).$$

The logarithm of the number of reservoir states is proportional to the reservoir entropy, so

$$\ln \rho = S_r(E_o - \Delta E, V_o - \Delta V, N_o)/k + \text{constant} .$$

Expanding to first order in the meter energy and volume we obtain

$$\ln \rho = - \left(\frac{\partial S_r}{\partial E_r} \right)_{V_r, N_r} \Delta E - \left(\frac{\partial S_r}{\partial V_r} \right)_{E_r, N_r} \Delta V .$$

Comparing with our previous expression for $\ln \rho$ we see that the pressure and temperature that appear in the meter's Gibbs distribution are related to the reservoir's entropy by the usual reservoir thermodynamic relations

$$\begin{aligned} \frac{1}{T} &= \left(\frac{\partial S_r}{\partial E_r} \right)_{V_r, N_r} , \\ P &= T \left(\frac{\partial S_r}{\partial V_r} \right)_{\tilde{E}_r, N_r} = \left(\frac{\partial \tilde{E}_r}{\partial S_r} \right)_{N_r, V_r} \left(\frac{\partial S_r}{\partial V_r} \right)_{\tilde{E}_r, N_r} = - \left(\frac{\partial \tilde{E}_r}{\partial V_r} \right)_{N_r, S_r} . \end{aligned}$$

In the last step we have used an obvious analog of Eq. (4) of Box 4.1.

B

Exercise 4.3 Enthalpy Representation of Thermodynamics [by Xinkai Wu]

(a) Combining $H = \tilde{E} + PV$ with the first law $d\tilde{E} = TdS - PdV + \tilde{\mu}dN$ one immediately finds $dH = VdP + TdS + \tilde{\mu}dN$. Having this expression we can compute $V, T, \tilde{\mu}$ by differentiating H w.r.t. P, S, N , respectively, namely H serves as the fundamental potential in this case.

(b) In the first law derived in part (a), there's dS , dN but no dV . Thus the only extensive quantities exchanged between the system and the bath are volume and energy; and the energy exchange is fixed completely by the volume exchange, $d\tilde{E} = -PdV$, i.e., it is entirely mechanical energy exchange. There is no exchange of heat and no exchange of particles. A physical situation which could produce this ensemble is: the system is put in a chamber, with a frictionless piston separating the system and the bath, where the walls and the piston are impermeable and heat-insulating.

(c) The equations of state read off from the enthalpy first law and the associated Maxwell relations are:

$$\begin{aligned} V &= \left(\frac{\partial H}{\partial P} \right)_{S,N}, \quad T = \left(\frac{\partial H}{\partial S} \right)_{P,N}, \quad \tilde{\mu} = \left(\frac{\partial H}{\partial N} \right)_{P,S} \\ \frac{\partial^2 H}{\partial P \partial S} &= \left(\frac{\partial V}{\partial S} \right)_{P,N} = \left(\frac{\partial T}{\partial P} \right)_{S,N} = \frac{\partial^2 H}{\partial S \partial P} \\ \frac{\partial^2 H}{\partial S \partial N} &= \left(\frac{\partial T}{\partial N} \right)_{P,S} = \left(\frac{\partial \tilde{\mu}}{\partial S} \right)_{P,N} = \frac{\partial^2 H}{\partial N \partial S} \\ \frac{\partial^2 H}{\partial N \partial P} &= \left(\frac{\partial \tilde{\mu}}{\partial P} \right)_{S,N} = \left(\frac{\partial V}{\partial N} \right)_{P,S} = \frac{\partial^2 H}{\partial P \partial N} \end{aligned}$$

(d) “adding up small subsystems”, we get

$$H = TS + \tilde{\mu}N$$

(e) In Exercise 2.4 it is shown that the inertial mass per unit volume is

$$\begin{aligned} \rho_{ji}^{inert} &= T^{00}\delta_{ji} + T_{ji} \\ \text{for isotropic system} \\ &= \rho\delta_{ji} + P\delta_{ji} = (\rho + P)\delta_{ij}. \end{aligned}$$

Thus the total inertial mass is isotropic and is given by $\rho V + PV = \tilde{E} + PV = H$.

(f) To create the sample, we need $\Delta\tilde{E}$, the sample's energy. To inject the sample into the system, we need to perform an amount of work $P\Delta V$ on the system. Thus the total energy required to create the sample and perform the injection is $\Delta\tilde{E} + P\Delta V$, which is just the sample's enthalpy. Thus, enthalpy has the physical interpretation of “energy of injection at fixed volume V ”.

Thermodynamic Manipulations [by Michael Cross]

(a) In an isolated expansion the internal energy E is conserved (not entropy, since this is not a reversible change). Thus we want

$$\left(\frac{\partial T}{\partial V} \right)_E = - \left(\frac{\partial E}{\partial V} \right)_T / \left(\frac{\partial E}{\partial T} \right)_V.$$

The thermodynamic identity for E is

$$dE = TdS - pdV$$

so

$$\left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - P = T \left(\frac{\partial P}{\partial T} \right)_V - P$$

(using a Maxwell identity in the second step), and

$$\left(\frac{\partial E}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V = C_V$$

and the result follows by simple algebra.

(b) In this case entropy is conserved, and so we want

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial S}{\partial V}\right)_T / \left(\frac{\partial S}{\partial T}\right)_V$$

Simply using the same Maxwell identity and $T(\partial S/\partial T)_V = C_V$ gives the result.

(c) For per particle of gas that passes through the porous plug the mechanical work done is $P_1 v_1 - P_2 v_2$ where v_1, v_2 are the volumes per particle V_1/N_1 etc. at the two pressures. Since there is no heat input this means $h = \varepsilon + Pv$ is preserved. Thus we want

$$\left(\frac{\partial T}{\partial P}\right)_h = -\frac{\left(\frac{\partial h}{\partial P}\right)_T}{\left(\frac{\partial h}{\partial T}\right)_P}.$$

The thermodynamic identity for h is (sing small letters for the densities $s = S/N$ etc.)

$$dh = Tds + vdP$$

and then

$$\left(\frac{\partial h}{\partial P}\right)_T = T\left(\frac{\partial s}{\partial P}\right)_T + v = -T\left(\frac{\partial v}{\partial T}\right)_P + v$$

where the Maxwell identity deriving from $dg = -sdT + vdP$ is used. Also

$$\left(\frac{\partial h}{\partial T}\right)_P = T\left(\frac{\partial s}{\partial T}\right)_P = C_P/N.$$

Using $\alpha_P = v^{-1}(\partial v/\partial T)_P$ gives the result.

C

Exercise 4.6 Saha Equation for Ionization Equilibrium [by Huan Yang]

(a) In chemical equilibrium, the sum weighted by stoichiometric coefficients of the chemical potentials of the reactants should be equal to the sum for products. Thus we have:

$$\tilde{\mu}_H + \tilde{\mu}_\gamma = \tilde{\mu}_e + \tilde{\mu}_p \text{ and } \tilde{\mu}_e + \tilde{\mu}_p = \tilde{\mu}_e + \tilde{\mu}_p + \tilde{\mu}_\gamma$$

$$\text{so } \tilde{\mu}_\gamma = 0 \text{ and } \tilde{\mu}_H = \tilde{\mu}_e + \tilde{\mu}_p.$$

(b) We have number density n_s which can be expressed by:

$$n_s = \frac{g_s}{Vh^3} \int d^3p d^3x \mathcal{N}$$

where g_s is the degeneracy of the state. In non-relativistic limit

$$\mathcal{N} = \exp\left(-\frac{E_s - \mu_s}{kT}\right) = \exp\left(-\frac{\frac{p^2}{2m} - (\tilde{\mu}_s - m_s c^2)}{kT}\right)$$

Plug it into the expression of n_s , we can get

$$n_s = \frac{g_s}{h^3} \exp\left(\frac{\tilde{\mu}_s - m_s c^2}{kT}\right) (2\pi m_s kT)^{3/2}$$

$s = H, e, p$ and $g_H = 4, g_e = 2, g_p = 2$

(c) Just directly computing $\frac{n_e n_p}{n_H}$ and note $(m_H - m_e - m_p)c^2 = -I$, we can easily get:

$$\frac{n_e n_p}{n_H} = \frac{(2\pi m_s kT)^{3/2}}{h^3} e^{-\frac{I}{kT}}$$

Exercise 4.5 Electron-Positron Equilibrium at “Low” Temperatures [by Xinkai Wu]

(a) The reaction equation $e^- + p \longrightarrow e^- + p + e^- + e^+$ gives $\tilde{\mu}_{e^-} + \tilde{\mu}_p = 2\tilde{\mu}_{e^-} + \tilde{\mu}_p + \tilde{\mu}_{e^+}$, which implies $\tilde{\mu}_{e^-} + \tilde{\mu}_{e^+} = 0$, i.e. $\tilde{\mu}_{e^-} = -\tilde{\mu}_{e^+}$.

(b) In what follows we shall use $\tilde{\mu}_-$ to denote $\tilde{\mu}_{e^-}$, and $\tilde{\mu}_+$ to denote $\tilde{\mu}_{e^+}$. The distribution function(density in phase space) for positrons and electrons (both having $g_s = 2$) is given by

$$\begin{aligned}\mathcal{N}_\pm &= \frac{2}{h^3} \eta_\pm = \frac{2}{h^3} \frac{1}{e^{(\tilde{E} - \tilde{\mu}_\pm)/kT} + 1} \\ \tilde{E} &\approx mc^2 + \mathbf{p}^2/2m \\ \Rightarrow \mathcal{N}_\pm &= \frac{2}{h^3} \frac{1}{e^{(\frac{\mathbf{p}^2}{2m} + mc^2 - \tilde{\mu}_\pm)/kT} + 1}\end{aligned}$$

The density in coordinate space n_\pm is given by $\int d^3\mathbf{p} \mathcal{N}_\pm$. We know that $n_- > n_+$ because while positrons and electrons are created in pairs we also have ionization electrons from hydrogen atoms. Thus we must have $\tilde{\mu}_- > \tilde{\mu}_+$. This inequality combined with $\tilde{\mu}_- + \tilde{\mu}_+ = 0$ gives $\tilde{\mu}_- > 0$, $\tilde{\mu}_+ < 0$.

(c) In the dilute-gas regime, $\eta_\pm \approx \exp\left[-\left(\frac{\mathbf{p}^2}{2m} + mc^2 - \tilde{\mu}_\pm\right)/kT\right]$. It's trivial to perform the momentum-space integral and find

$$n_\pm = \frac{2}{h^3} (2\pi mkT)^{3/2} \exp\left(\frac{\tilde{\mu}_\pm - mc^2}{kT}\right)$$

$\eta \ll 1$ means $(\tilde{\mu}_\pm - mc^2) \ll -kT$ (see Chapter 2), i.e.

$$n_\pm \ll \frac{2}{h^3} (2\pi mkT)^{3/2} = 4.8 \times 10^{27} \left(\frac{T}{10^8 K}\right)^{3/2} \text{ cm}^{-3}$$

The hydrogen mass density is $\rho \approx n_- m_p$ (because $m_e \ll m_p$ and also electron-positron pair generation is negligible.) Thus the dilute-gas region is given by

$$\rho \ll 8 \times 10^3 \left(\frac{T}{10^8 K}\right)^{3/2} \text{ g} \cdot \text{cm}^{-3}$$

(d) Define $x \equiv e^{\tilde{\mu}_-/kT}$, then $e^{\tilde{\mu}_+/kT} = 1/x$. And using the expression for n_\pm we found in part (c), we get

$$n = n_- - n_+ = \frac{2}{h^3} (2\pi mkT)^{3/2} e^{-mc^2/kT} (x - 1/x)$$

$$\text{define } y \equiv \frac{1}{4} n \lambda^3 e^{mc^2/kT}, \text{ where } \lambda \equiv \frac{h}{\sqrt{2\pi mkT}}$$

$$\Rightarrow 2y = (x - 1/x)$$

$$\Rightarrow x = y + (1 + y^2)^{1/2}$$

$$\text{Thus } \frac{n_+}{n} = \frac{1/x}{x - 1/x} = \frac{1}{2y [y + (1 + y^2)^{1/2}]}$$

(e) [this part by Kip Thorne] The amount of phase space available to the ionization electrons, per ionization electron, is of order $V_{\text{phase}} \sim (2\pi mkT)^{3/2} \frac{m_p}{\rho}$. If one pair forms per ionization electron (our criterion for significant pair formation), then each positron will also have available to it the phase volume V_{phase} . When this V_{phase} is very large (i.e. when ρ is very small, at fixed $T \sim 10^8 K$), then the positron is almost completely unaware of the presence of the electrons, so the probability of its meeting an electron and annihilating is very small. This means that, although pair production occurs only very rarely (because of the very few number of photons with sufficient energy to produce a pair), once it has occurred, on average the positron lives for a very long time. It is this balancing of the long life, due to the huge phase space

per particle, against the rarity of pair production, that enables significant pairs to form at T as low as $\sim 10^8 K$.

D

Exercise 4.4 Latent Heat and the Clausius-Clapeyron Equation [by Xinkai Wu]

(a) For fixed temperature and pressure, the change in the Gibbs potential is

$$dG = \tilde{\mu}_a dN_a + \tilde{\mu}_b dN_b = (\tilde{\mu}_a - \tilde{\mu}_b) dN_a$$

where N_a is the number of particles in phase a etc., and we've used the fact that $dN_b = -dN_a$. By the minimum principle for the Gibbs potential, in equilibrium one must have $\tilde{\mu}_a = \tilde{\mu}_b$ (subtracting $m_{H_2O}c^2$ from both sides one finds $\mu_a = \mu_b$.)

The Gibbs potential G is a function of (T, P, N) , so the chemical potential $\mu = (\partial G / \partial N)_{T,P}$ is also a function of (T, P, N) . However, μ is an intensive quantity and consequently can't depend on the extensive quantity N , since the other two variables are intensive. This means that μ is a unique function of T and P . We also saw this in class as the Gibbs-Duhem expression.

In a two-phase region, we must have $\mu_a(T, P) = \mu_b(T, P)$, which is one equation for two variables T and P , giving a line in the $T - P$ plane. In a three-phase region, $\mu_a(T, P) = \mu_b(T, P)$, and $\mu_b(T, P) = \mu_c(T, P)$, which are two equations for the two variables T and P , giving a point in the $T - P$ plane.

(b) The melting curve $P = P(T)$ is determined by $\mu_{ice}(T, P) = \mu_{water}(T, P)$. For each phase, the thermodynamic identity for G/N or the Gibbs-Duhem relation for μ is

$$d\mu = -s dT + v dP,$$

with s and v the entropy and volume per particle. Subtracting this expression across adjacent points on the melting curve and using the result from equilibrium $d(\mu_{ice} - \mu_{water}) = 0$ gives

$$\left(\frac{dP}{dT}\right)_{\text{melt}} = \frac{s_{\text{water}} - s_{\text{ice}}}{v_{\text{water}} - v_{\text{ice}}}.$$

Using $s_{\text{water}} - s_{\text{ice}} = T \Delta q_{\text{melt}}$ and $v = 1/\rho$ gives the stated result.

(c) In equilibrium we still have $\mu_{\text{water}}(T, P_{\text{water}}) = \mu_{\text{vapor}}(T, P_{\text{vapor}})$. However, now P_{water} is no longer equal to P_{vapor} . Instead, $P_{\text{water}} = P_{\text{total}} = P_{\text{vapor}} + P_{\text{gas}}$. So we have $\mu_{\text{water}}(T, P_{\text{total}}) = \mu_{\text{vapor}}(T, P_{\text{vapor}})$. Fixing T and differentiating the above identity w.r.t. P_{total} , we have

$$\begin{aligned} \left(\frac{\partial \mu_{\text{water}}}{\partial P_{\text{total}}}\right)_T &= \left(\frac{\partial \mu_{\text{vapor}}}{\partial P_{\text{vapor}}}\right)_T \left(\frac{dP_{\text{vapor}}}{dP_{\text{total}}}\right)_T \\ \Rightarrow \left(\frac{dP_{\text{vapor}}}{dP_{\text{total}}}\right)_T &= \left(\frac{\partial \mu_{\text{water}}}{\partial P_{\text{total}}}\right)_T / \left(\frac{\partial \mu_{\text{vapor}}}{\partial P_{\text{vapor}}}\right)_T \\ &= \rho_{\text{vapor}} / \rho_{\text{water}} \end{aligned}$$

Note that the Gibbs-Duhem result applies only to single component regions i.e., for the liquid we have $(\partial \mu_{\text{water}} / \partial P_{\text{total}})_T = v_{\text{water}}$. For the vapor phase we assume the gases are ideal, so that the presence of the second gas does not affect the equation of state of the first gas, and so $(\partial \mu_{\text{vapor}} / \partial P_{\text{vapor}})_T = v_{\text{vapor}}$.

Exercise 4.9 One Dimensional Ising Lattice [by Jeff Atwell]

(a) Suppose that we have N dipoles lined up. Label the spins s_1, \dots, s_N . Using the notation of equation (4.55), the total energy is

$$E = -kTK (s_1 s_2 + s_2 s_3 + \dots + s_{N-1} s_N).$$

Then the partition function will be

$$z(N, K) = \sum_{s_1, \dots, s_N} e^{K(s_1 s_2 + \dots + s_{N-1} s_N)}.$$

This is all that is required for part (a).

(b) Now explicitly sum over the odd spins

$$z(N, K) = \sum_{s_2, s_4, \dots} \dots [e^{K(s_2+s_4)} + e^{-K(s_2+s_4)}] [e^{K(s_4+s_6)} + e^{-K(s_4+s_6)}] \dots$$

(Ignore any subtleties occurring at the endpoints of the line segment. These effects are insignificant for large N . If this really bothers you, you can use “periodic boundary conditions” in which a $s_1 s_N$ interaction term is added. In this case the issue disappears completely.) Now we would like to rewrite the first term in square brackets in a form involving nearest-neighbor interactions of the even spins:

$$[e^{K(s_2+s_4)} + e^{-K(s_2+s_4)}] = f(K)e^{K's_2 s_4}.$$

Our job is to now find $f(K)$ and $K'(K)$. This equation must hold for $s_2, s_4 = 1, -1$. Set $s_2 = s_4 = +1$ to find

$$e^{2K} + e^{-2K} = 2 \cosh(2K) = f(K)e^{K'}. \quad (1)$$

Set $s_2 = +1$ and $s_4 = -1$ to find

$$2 = f(K)e^{-K'}. \quad (2)$$

Divide equation (1) by equation (2) to find $\cosh(2K) = e^{2K'}$, or $K' = \frac{1}{2} \ln[\cosh(2K)]$. Now substitute this value of K' back into equations (1) and (2):

$$2 \cosh(2K) = f(K) [\cosh(2K)]^{1/2},$$

and

$$2 = f(K) [\cosh(2K)]^{-1/2}.$$

Now one sees that $f(K) = 2 [\cosh(2K)]^{1/2}$ will solve both equations. So finally we have

$$z(N, K) = \sum_{s_2, s_4, \dots} \dots [f(K)e^{K's_2 s_4}] [f(K)e^{K's_4 s_6}] \dots = f(K)^{N/2} z(N/2, K').$$

(c) Recall that K depends on the temperature T . From the discussion in Chapter 4, we know that the phase transition will be at the temperature which corresponds to a fixed point of the iterative map, i.e. when $K' = K$. So we need to look for numerical solutions to

$$K = \frac{1}{2} \ln[\cosh(2K)],$$

in the range $K > 0$. However plotting the two sides shows that there are no solutions in this region, and so there is no phase transition.

E

Phase Transitions in a Van der Waals Gas [by Michael Cross]

(a) The pressure is $P = -(\partial F/\partial V)_{T,N}$ and $P_{ideal} = Nk_B T/V$ so that

$$P = \frac{Nk_B T}{V} + \frac{Nk_B T}{V} \frac{Nb}{V - Nb} - \frac{N^2 a}{V^2} \quad (3)$$

or

$$\left(P + \frac{N^2 a}{V^2}\right) (V - Nb) = Nk_B T \quad (4)$$

(b) One needs to solve the equation $\left(\frac{\partial P}{\partial V}\right)_T = 0$ for v . One finds that for $T < T_{crit}$, there are two solutions V_1, V_2 (namely there's a local maximum and a local minimum); when $T = T_{crit}$, V_1 and V_2 merge into a

single V_{crit} ; and when $T > T_{crit}$, there's no solution. Now let's determine T_{crit} and V_{crit} . At T_{crit} , V_{crit} , we have

$$0 = \left(\frac{\partial P}{\partial V} \right)_T = \frac{-Nk_B T}{(V - Nb)^2} + \frac{2N^2 a}{V^3} \quad 0 = \left(\frac{\partial^2 P}{\partial^2 V} \right)_T = \frac{2Nk_B T}{(V - Nb)^3} - \frac{6N^2 a}{V^4} \quad (5)$$

Combining the above two equations, we find $k_B T_{crit} = 8Na/27b$, and $V_{crit} = 3Nb$.

(c) At constant temperature the Helmholtz free energy F *decreases* in the relaxation towards equilibrium. Thus the condition for stability (no spontaneous motion of a “division” between two halves of a system) is

$$2F(V) \leq F(V + \Delta V) + F(V - \Delta V). \quad (6)$$

Geometrically, any chord must lie above the curve—the Helmholtz free energy $F(V)$ is a concave function of V . Writing $F(V \pm \Delta V)$ using the Taylor expansion:

$$F(V \pm \Delta V) = F(V) + (\Delta V) \left(\frac{\partial F}{\partial V} \right)_T + \frac{(\Delta V)^2}{2!} \left(\frac{\partial^2 F}{\partial V^2} \right)_T + \dots, \quad (7)$$

the inequality Eq. (6) becomes

$$\left(\frac{\partial^2 F}{\partial V^2} \right)_T \geq 0. \quad (8)$$

The pressure P of the system is

$$P \equiv - \left(\frac{\partial F}{\partial V} \right)_T. \quad (9)$$

So, the condition on the second derivative implies that

$$\left(\frac{\partial P}{\partial V} \right)_T \leq 0. \quad (10)$$

Thermodynamically (and intuitively), this condition means that the system expands when pressure on it is released. If this were not the case, the system would be linearly unstable.

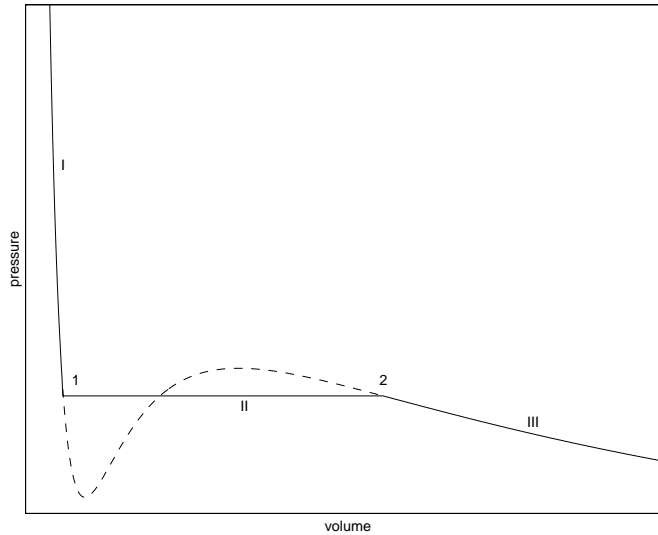


Figure 1: The PV isotherm calculated for the van der Waals equation.

(c) From Eq. (9),

$$F(V) = - \int^V P(v) dv \quad (11)$$

so the Helmholtz free energy $F(V)$ is the negative of the integral of the PV isotherm. A sketch of the curve of $F(V)$ is shown in Fig. 2. The solid-dashed-solid portion corresponds to the smooth van der Waals curve. The flat line must be chosen to give the unique common tangent in the $F(V)$ curve. This condition uniquely defines the Maxwell construction in the $P - V$ plot.

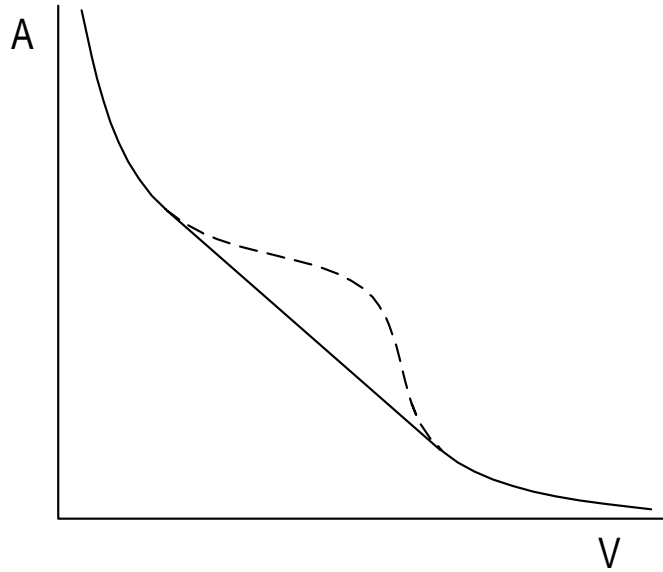


Figure 2: Sketch of the Helmholtz free energy A as a function of volume V .

(d) Referring to Fig. 1, region I corresponds to the liquid state, because the slope is relatively large, so that the compressibility (change in volume per unit change in pressure) of this region is relatively small, as would be the case for the liquid state. Region III corresponds to the gaseous state. In region II, both the liquid and gas co-exist in equilibrium.

(e) Using the “slope-intercept” method, the Gibbs free energy G is plotted as a function of P in Fig. 3. The curve’s slope is discontinuous at the point P_M , which is where region II gets mapped into. Note that both regions I and III are *concave* now, because the Legendre transformation from F to G changes the sign of the second derivative. Alternatively, the concavity of the Gibbs free energy can be seen by writing

$$G = F + PV = E - TS + PV. \quad (12)$$

At constant T and constant E ,

$$dG = V dP. \quad (13)$$

Thus,

$$\frac{\partial^2 G}{\partial P^2} = \frac{\partial V}{\partial P} \leq 0 \quad (14)$$

from Eq. (10). Thus, G is concave.

(f) From the above construction, a transition from point 1 (liquid state) to point 2 (gaseous state) in Fig. 1 corresponds to no change in Gibbs free energy, i.e.,

$$G(2) - G(1) = \int_1^2 dG = 0. \quad (15)$$

From Eq. (13),

$$\int_1^2 V dP = 0. \quad (16)$$

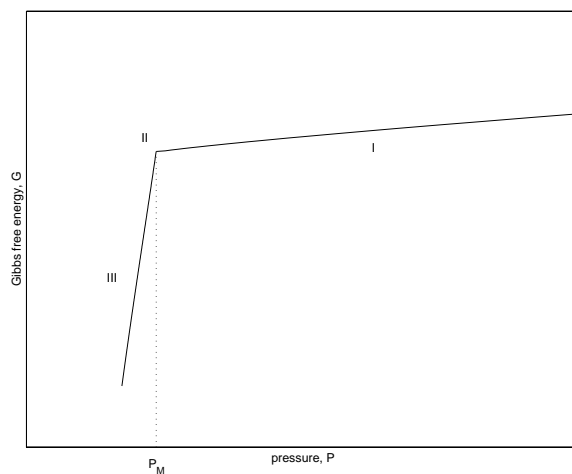


Figure 3: The Gibbs free energy G as a function of pressure P .

This means that the line integral of V with respect to P , taken from point 1 to point 2, is zero, i.e., the areas $A + B = 0$, or area $A = \text{area } B$; see Fig. 4. This is Maxwell's "equal-area" construction: P_M is chosen such that the area of the dashed curve above the P_M line is equal in magnitude to that under the line.

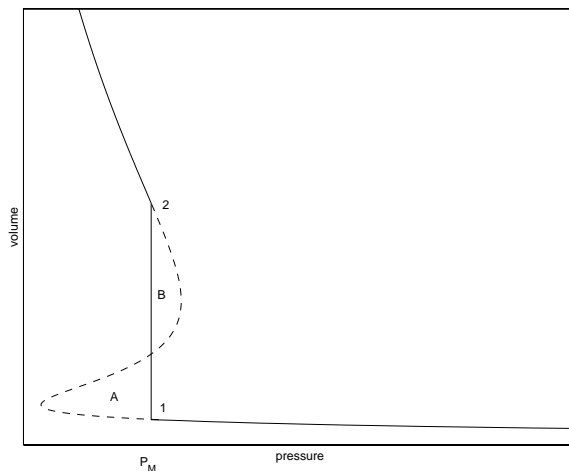


Figure 4: Line integral of V with respect to P from point 1 to 2.